

Depletion potential in colloidal mixtures of hard spheres and platelets

L. Harnau and S. Dietrich

*Max-Planck-Institut für Metallforschung, Heisenbergstrasse 3, D-70569 Stuttgart, Germany**and Institut für Theoretische und Angewandte Physik, Universität Stuttgart, Pfaffenwaldring 57, D-70569 Stuttgart, Germany*

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The depletion potential between two hard spheres in a solvent of thin hard disclike platelets is investigated by using either the Derjaguin approximation or density functional theory. Particular attention is paid to the density dependence of the depletion potential. A second-order virial approximation is applied, which yields nearly exact results for the bulk properties of the hard-platelet fluid at densities two times smaller than the density of the isotropic fluid at isotropic-nematic phase coexistence. As the platelet density increases, the attractive primary minimum of the depletion potential deepens and an additional small repulsive barrier at larger sphere separations develops. Upon decreasing the ratio of the radius of the spheres and the platelets, the primary minimum diminishes and the position of the small repulsive barrier shifts to smaller values of the sphere separation.

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I. INTRODUCTION

Depletion interactions between big colloidal particles induced by smaller particles, which can be either the solvent particles or a colloidal component of its own, are of significant current research interest because of the importance of these effective interactions in various colloidal processes. For example, flocculation of colloids can be driven by the addition of nonadsorbing polymers via the depletion mechanism [1]. Whereas experimental and theoretical studies have focussed on binary hard-sphere fluids as well as on colloidal mixtures of hard spheres and hard rods or polymers, less attention has been paid to hard platelets acting as depletants, despite the great importance of colloidal platelets such as blood platelets and clay minerals in both biomedicine and geophysics. Very recently a colloidal mixture of silica spheres and silica coated gibbsite platelets has been stabilized for the first time [2], and the depletion potential due to the presence of thin hard platelets has been derived theoretically for noninteracting platelets corresponding to the limit of infinite dilution [2,3]. It has been found that the Derjaguin approximation for the depletion potential yields accurate results for noninteracting platelets provided the ratio of the radius of the spheres and the platelets is large [2].

In this paper we focus on the depletion interaction induced by thin hard platelets, taking into account the steric interactions between the platelets in terms of a second-order virial approximation. On the basis of our recent theoretical studies on fluids of thin hard platelets near hard walls [4,5], we expect that excluded volume interactions between the platelets influence the depletion interaction already at rather low platelet densities due to their cumbrous shape as compared with spherical or rodlike depletants. Taking excluded volume interactions into account is particularly interesting because correlation effects may cause repulsive features of depletion forces which are important in the context of colloidal stability [6]. In the present paper we use density functional theory (Sec. II) to study the depletion potential between two hard spheres induced by thin hard platelets (Sec. III). Particularly, we compare the results with the ones obtained for noninteracting platelets.

II. DENSITY FUNCTIONAL THEORY

We consider an inhomogeneous fluid consisting of thin platelets of radius R_p in a container of volume V . The platelets are taken to be hard discs without additional attractive or repulsive interactions. The number density of the centers of mass of the platelets at a point \mathbf{r} with an orientation $\omega = (\theta, \phi)$ of the normal of the platelets is denoted by $\rho(\mathbf{r}, \omega)$. The equilibrium density profile of the inhomogeneous liquid under the influence of an external potential $V(\mathbf{r}, \omega)$ minimizes the grand potential functional

$$\Omega[\rho(\mathbf{r}, \omega)] = \int dr^3 d\omega \rho(\mathbf{r}, \omega) [k_B T (\ln[4\pi\Lambda^3 \rho(\mathbf{r}, \omega)] - 1) - \mu + V(\mathbf{r}, \omega)] + F_{ex}[\rho(\mathbf{r}, \omega)], \quad (1)$$

where Λ is the thermal de Broglie wavelength and μ is the chemical potential. The free energy functional $F_{ex}[\rho(\mathbf{r}, \omega)]$ in excess of the ideal gas contribution has not been taken into account in previous studies on the depletion force due to platelets [2,3]. We express the excess free energy functional as an integral over all possible configurations of two platelets

$$F_{ex}[\rho(\mathbf{r}, \omega)] = -\frac{k_B T}{2} \int dr_1^3 d\omega_1 dr_2^3 d\omega_2 \rho(\mathbf{r}_1, \omega_1) \times f_{pp}(\mathbf{r}_{12}, \omega_1, \omega_2) \rho(\mathbf{r}_2, \omega_2), \quad (2)$$

where $\mathbf{r}_{12} = \mathbf{r}_1 - \mathbf{r}_2$ and $f_{pp}(\mathbf{r}_{12}, \omega_1, \omega_2)$ is the Mayer function of the interaction potential between two platelets. The Mayer function equals -1 if the platelets overlap and is zero otherwise. Explicit expressions of the Mayer function for thin platelets are documented in Refs. [4,7].

For the homogeneous and isotropic bulk fluid the grand potential functional [Eq. (1)] reduces to

$$\frac{\Omega_b}{V} = \rho_b [k_B T (\ln[\Lambda^3 \rho_b] - 1) - \mu] + \frac{\pi^2}{2} R_p^3 \rho_b^2 k_B T, \quad (3)$$

where $\rho_b = V^{-1} \int dr^3 d\omega \rho(\mathbf{r}, \omega)$ is the total particle number density. The equation of state derived from the grand potential [Eq. (3)] takes the following form:

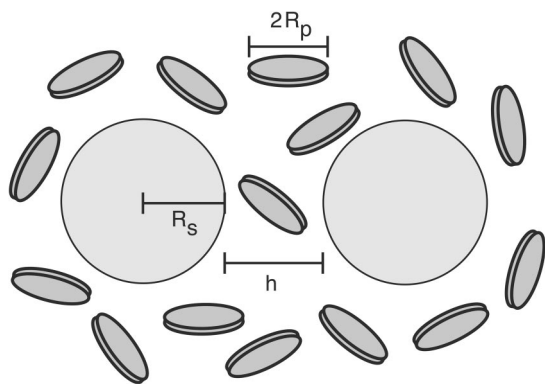


FIG. 1. The system under consideration consists of two hard spheres of radius R_s immersed in a solvent of hard platelets of radius R_p . The separation between the surfaces of the spheres is denoted by h . Only the projection of the spheres on the plane of the figure is shown.

$$p_b^* = \rho_b^* \left(1 + \frac{\pi^2}{2} \rho_b^* \right) \quad (4)$$

with $\rho_b^* = \rho_b R_p^3$ and $p_b^* = p_b R_p^3 / (k_B T)$. The same equation without the second term in parenthesis holds for the ideal gas limit (i.e., noninteracting platelets). With increasing particle number density the ideal gas equation of state on one side and the second-term virial series [Eq. (4)] as well as computer simulation data [7–9] on the other side deviate. Thus for $\rho_b^* = 0.1$ the osmotic pressure $p_b^* = 0.15$, as calculated from Eq. (4), agrees exactly with simulation data, while the ideal gas equation of state underestimates the osmotic pressure by a factor of 1.5. The comparison of the calculated equation of state with computer simulation data exhibits that the two-term series in Eq. (4) is a good approximation for $\rho_b^* \leq 0.2$, whereas the ideal gas model may be used for very low particle number densities $\rho_b^* \leq 0.04$. For a discussion of higher-order virial terms for fluids consisting of hard platelets we refer to Refs. [4,10–12]. In the present study we restrict our attention to particle number densities $\rho_b^* \leq 0.2$ for which the second-order virial approximation is appropriate and the platelet fluid is in the isotropic phase. For comparison, the isotropic-nematic phase transition is first order with coexistence densities $\rho_{bI} R_p^3 = 0.46$ and $\rho_{bN} R_p^3 = 0.5$ according to a computer simulation [9].

III. THE PLATELET-INDUCED DEPLETION POTENTIAL BETWEEN TWO SPHERES

The results of the preceding section show that intermolecular interactions between platelets increase the osmotic pressure of the bulk fluid already at low particle densities. Now we study the influence of intermolecular interactions on the depletion potential between two hard spheres of radius R_s immersed in a fluid of hard platelets of radius R_p . The depletion potential $W(h)$ is the free energy difference between the configurations of two big spheres at fixed distance h im-

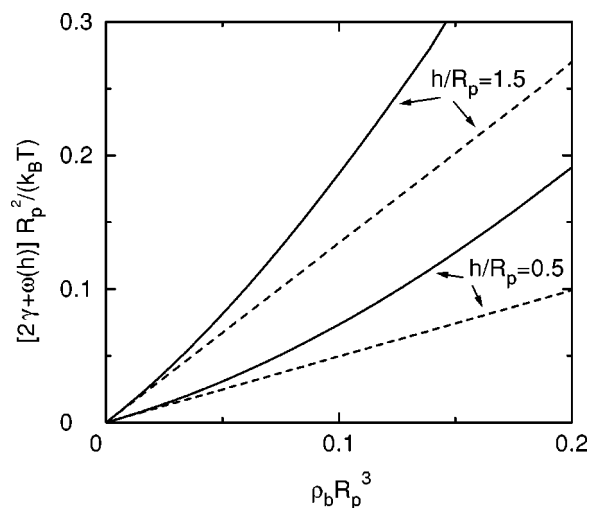


FIG. 2. The surface and finite-size contribution $2\gamma + \omega(h)$ to the grand potential as obtained from Eqs. (1), (2), and (6) (solid lines) of a fluid consisting of thin hard platelets of radius R_p confined in a slit of width h and in contact with an isotropic bulk reservoir at density ρ_b . The dashed lines represent the corresponding results for an ideal gas of platelets [see Eq. (7)]. The width of the slit increases from bottom to top: $h/R_p = 0.5, 1.5$.

mersed in the solvent and at macroscopic separation $h = \infty$ (see Fig. 1).

A. The Derjaguin approximation

The depletion potential $W(h)$ between two hard spheres at close distance due to the presence of small platelets ($R_p \ll R_s$) can be calculated from the finite-size contribution of the grand potential function $\omega(h')$ of the platelet fluid confined between two parallel hard walls at distance h' using the Derjaguin approximation [13]

$$W_{Derj}(h) = \pi R_s \int_h^\infty dh' \omega(h'), \quad (5)$$

where h is the separation between the surfaces of the spheres. (For the subtle issue of the range of validity of the Derjaguin approximation see Refs. [14,15].)

We first consider a hard-platelet fluid confined by two parallel hard walls at $z=0$ and $z=h$, and calculate the surface and finite size contributions to the grand potential defined via

$$\Omega[\rho(z, \theta, \phi)] = V\omega_b + 2A\gamma + A\omega(h), \quad (6)$$

where A is the area of a single surface, ω_b is the bulk grand canonical potential density, and V is defined as the volume of the container with its surface given by the position of the rim of the particles at closest approach so that $V = Ah$. γ is the wall-liquid surface tension in the absence of the second wall and $\omega(h)$ is the finite-size contribution. Figure 2 displays the calculated surface and finite-size contributions to the grand potential together with the results for noninteracting platelets [2,3]

$$\frac{[2\gamma + \omega(h)]_{ideal}}{k_B T} = \begin{cases} \rho_b R_p \left[\arcsin\left(\frac{h}{2R_p}\right) + \frac{h}{2R_p} \sqrt{1 - \left(\frac{h}{2R_p}\right)^2} \right], & 0 \leq h \leq 2R_p \\ \frac{\pi}{2} \rho_b R_p = \frac{2\gamma_{ideal}}{k_B T}, & h \geq 2R_p. \end{cases} \quad (7)$$

As is apparent from Fig. 2 the steric interaction between the platelets increases the surface contributions with increasing density. Within our numerical precision, we found that an accurate evaluation of the wall-liquid surface tension γ could be achieved for a fixed wall separation $h=4R_p$ at all considered densities $\rho_b R_p^3 \leq 0.2$. For much higher densities, a larger value of h might be required because of the wetting of the wall-isotropic liquid interface by a nematic film of diverging thickness [5]. On the other hand the wall-liquid surface tension $\gamma_{ideal}/(k_B T) = \rho_b R_p \pi/4$ for noninteracting platelets follows from Eq. (7) for a wall separation $h=2R_p$. For a detailed discussion of the surface tension and the excess coverage as well as the density and orientational order parameter profiles of fluids consisting of thin hard platelets near a single hard wall we refer to Ref. [4]. The results for the finite-size contribution $\omega(h)$ are shown in Fig. 3(a). As function of h the finite-size contribution corresponds to the solvation free energy for the immersed two plates acting as the confining walls for the fluid and, by construction, $\omega(0)$

$= -2\gamma$ and $\omega(\infty)=0$. Upon increasing the platelet density, the attractive minimum of $\omega(h)$ at $h=0$ deepens and a maximum at larger values of h develops. The corresponding solvation force per unit area $f(h) = -d\omega(h)/dh$ is attractive for small slit widths h as is shown in Fig. 3(b). Upon increasing the platelet density, the cusp of the solvation force at $h=2R_p$ sharpens. For comparison we note that the maximum at the cusp is more pronounced for the confined platelet fluid than for a corresponding rod fluid [6] due to the relatively larger steric interactions between platelets as compared with those between rods. Moreover $f(h)$ is a convex function for slit widths smaller than two times the radius of the platelets, while the solvation force in a solvent of hard rods is a concave function for slit widths smaller than the length of the rods [6]. Figure 4 displays the depletion potential together with the results for noninteracting platelets which can be calculated analytically from Eqs. (5) and (7) [2,3]:

$$\frac{W_{Derj}^{(ideal)}}{k_B T} = \begin{cases} -\pi \rho_b R_p^2 R_s \left(\frac{h}{R_p} \arcsin\left(\frac{h}{2R_p}\right) + \frac{4}{3} \sqrt{1 - \left(\frac{h}{2R_p}\right)^2} \left(1 + \frac{h^2}{8R_p^2}\right) - \frac{\pi h}{2R_p} \right), & 0 \leq h \leq 2R_p \\ 0, & h \geq 2R_p. \end{cases} \quad (8)$$

The depletion potential due to the presence of interacting platelets exhibits a small barrier at larger sphere separations h in addition to the primary minimum at $h=0$. With increasing platelet density the depletion potential deepens and the position of the maximum shifts to smaller values of h . The small repulsive barrier will have minor effects on kinetic stabilization, although the repulsive features might still be measurable. For example, our numerical calculations exhibit a maximum barrier height of $0.25k_B T$ relative to zero at a density of $\rho_b R_p^3 = 0.2$ in a system of size ratio $R_s/R_p = 3.5$ corresponding to the aforementioned mixture of silica spheres and gibbsite platelets [2]. In order to examine the influence of steric interactions between platelets on thermodynamic properties of sphere-platelet mixtures, we treat the depletion potential as a perturbation to the hard-sphere potential. The first-order approximation in this thermodynamic

perturbation approach for the Helmholtz free energy per sphere is

$$f(\rho_s, \rho_b) = f^{(hs)}(\rho_s) + 2\pi\rho_s \int_{2R_s}^{\infty} dr r^2 W(r - 2R_s) g^{(hs)}(r, \rho_s), \quad (9)$$

where $g^{(hs)}(r, \rho_s)$ is the radial distribution function of the pure sphere fluid and $f^{(hs)}(\rho_s)$ is the Helmholtz free energy per sphere for the same homogeneous fluid of density ρ_s . In the limit $R_s \gg R_p$ the radial distribution function $g^{(hs)}(r, \rho_s)$ is almost constant over the range of integration where $W(r - 2R_s) \neq 0$ and we can approximate it by its constant contact value $g^{(hs)}(2R_s, \rho_s)$ [16]. Using Eq. (8) the resulting integral

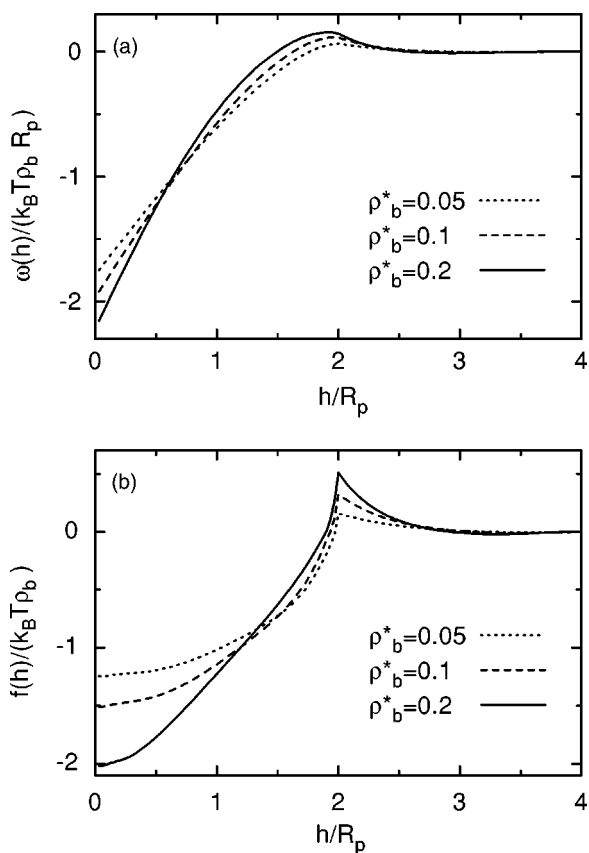


FIG. 3. (a) The finite-size contribution $\omega(h)$ to the grand potential as obtained from Eqs. (1), (2), and (6) of a fluid consisting of thin hard platelets of radius R_p confined in a slit of width h for three values of the density of the isotropic bulk reservoir: $\rho_b^* = \rho_b R_p^3 = 0.05$ (dotted line); $\rho_b^* = 0.1$ (dashed line); $\rho_b^* = 0.2$ (solid line). (b) The solvation force per unit area $f(h) = -d\omega(h)/dh$ of the same fluid [with the same line code as in (a)] as a function of h .

in Eq. (9) can be evaluated analytically for noninteracting platelets:

$$A_{Derj}^{(ideal)} \equiv 2\pi\rho_s \int_{2R_s}^{\infty} dr r^2 \frac{W_{Derj}^{(ideal)}(r-2R_s)}{k_B T} = -2\pi^2 \rho_b R_p^3 \rho_s R_s^3 \left(\pi + \frac{64 R_p}{45 R_s} + \frac{\pi R_p^2}{12 R_s^2} \right). \quad (10)$$

The integrated strength of the depletion potential $A_{Derj}^{(ideal)}$ is negative, reflecting the fact the depletion potential is always attractive (Fig. 4). A numerical calculation of the corresponding quantity A_{Derj} for interacting platelets exhibits that the steric interacting between the platelets weakens the integrated strength of the depletion potential by 22% at a bulk density $\rho_b R_p^3 = 0.2$. Hence the influence of steric interactions between platelets might be quite visible for phase equilibria. For example, the thermodynamic onset of flocculation of colloidal spheres induced by the depletion effect will be reduced due to platelet interactions.

In order to elucidate a possible depletion induced phase separation, we have calculated the second virial coefficient of the fluid mixture according to $B_2 = B_2^{(HS)} + 2\pi \int_{2R_s}^{\infty} dr r^2 (1$

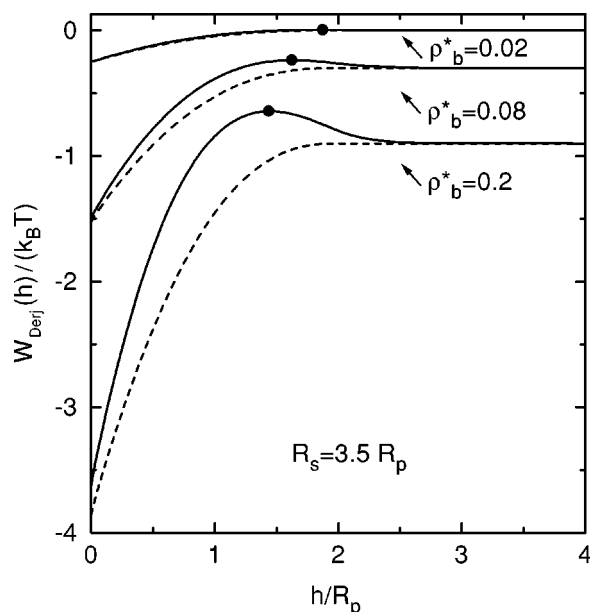


FIG. 4. Depletion potential $W_{Derj}(h)$ between two hard spheres of radius $R_s = 3.5R_p$ due to the presence of thin hard platelets of radius R_p as obtained from the Derjaguin approximation [Eq. (5)] for various bulk densities ρ_b of the platelets: $\rho_b^* = \rho_b R_p^3 = 0.02$ (top curves); $\rho_b^* = 0.08$ (middle curves); $\rho_b^* = 0.2$ (bottom curves). The solid lines (with dots marking the maxima) represent the calculations for interacting platelets and the dashed lines denote the results for noninteracting platelets. For reasons of clarity, the lower four curves are shifted down by $-0.3k_B T$ and $-0.9k_B T$, respectively. The dashed lines are zero for $h/R_p \geq 2$. Although the interactions have only minor influence on the depth of the primary minimum, the depletion potential becomes significantly less attractive for increasing densities ρ_b . This weakens the platelet induced flocculation of a solution of big spheres.

$-\exp[-W(r-2R_s)/(k_B T)]$), where $B_2^{(HS)} = 16\pi R_s^3/3$ is the second virial coefficient of the pure hard-sphere system. With increasing platelet density, the second virial coefficient exhibits a change of sign, signalling the possibility of a gas-liquid coexistence of a “liquid phase” rich in spheres (poor in platelets) and a “gas phase” that is poor in spheres (rich in platelets) in agreement with a recent free-volume scaled-particle approach [17].

B. Density functional approach

A general approach for calculating the depletion potential is based on a density functional theory (DFT) for a mixture of hard spheres and the particles acting as depletants [18,19]. This approach avoids the Derjaguin approximation. The depletion potential $W(\mathbf{r})$ is defined as the difference of the grand potential between a configuration in which the sphere acting as test particle is in the vicinity of another fixed sphere and one in which the former sphere is deep in the bulk. This grand potential difference can be expressed in terms of the difference of one-body direct correlation functions:

$$\frac{W(\mathbf{r})}{k_B T} = c_s^{(1)}(\infty) - c_s^{(1)}(\mathbf{r}). \quad (11)$$

DFT provides a route to the depletion potential since

$$c_s^{(1)}(\mathbf{r}) = -\frac{1}{k_B T} \frac{\partial F_{ex}[\rho_b, \rho_s]}{\partial \rho_s(\mathbf{r})}, \quad (12)$$

where $F_{ex}[\rho_b, \rho_s]$ is the free energy functional in excess of the ideal gas contribution to the grand potential of the platelet-sphere mixture and $\rho_s(\mathbf{r})$ denotes the number density of the spheres. For a given functional $F_{ex}[\rho_b, \rho_s]$, one can obtain the depletion potential from the one-body direct correlation function in the limit of vanishing density of the spheres. While for a binary hard sphere mixture a reliable fundamental measure functional is available [18], at present there is no similarly successful functional known for a platelet-sphere mixture at arbitrary number densities. In view of this state of the art we use the exact low-density, second-virial functional $F_{ex}[\rho_b, \rho_s]$ [19], which leads to the following approximate expression for the depletion potential:

$$-\frac{W(\mathbf{r})}{k_B T} = \int d\mathbf{r}_1^3 d\omega [\rho(\mathbf{r}_1, \omega) - \rho(\infty, \omega)] f_{sp}(\mathbf{r} - \mathbf{r}_1, \omega), \quad (13)$$

where $f_{sp}(\mathbf{r} - \mathbf{r}_1, \omega)$ is the Mayer function of the interaction potential between a sphere and a platelet. The Mayer function equals -1 if the particles intersect or touch each other and is zero otherwise. $\rho(\mathbf{r}_1, \omega)$ is the density profile of platelets in the external potential of a *single* fixed hard sphere located at the origin of the coordinate system and $\rho(\infty, \omega)$ is the corresponding density profile of the bulk fluid. We emphasize that the density profile entering Eq. (13) depends only on equilibrium properties of the depletant fluid in the *absence* of the second hard sphere to be inserted at position \mathbf{r} . This observation simplifies the calculation of $W(\mathbf{r})$ considerably, because the symmetry of the density profile is determined solely by the symmetry of the external potential of a single sphere fixed at the origin of the coordinate system.

Apart from possible surface freezing at high densities, nonuniformities of the density depend only on the radial distance $r = |\mathbf{r}|$, so that $\rho(\mathbf{r}, \omega) = \rho(r, \omega)$. Hence, calculating density profiles before insertion of the second hard sphere is much easier than after insertion, when the presence of the second sphere leads to a more complex spatial variation of the densities. A detailed discussion of Eq. (13) and its application to the analogous case of noninteracting hard rods acting as depletants is given in Ref. [19].

For an ideal gas of platelets in contact with a fixed hard sphere the density profile reduces to $\rho(r_1, \omega) - \rho(\infty, \omega) = \rho(\infty, \omega) f_{sp}(r_1, \omega)$ so that the integral in Eq. (13) has a purely geometrical meaning and measures the excluded volume of a platelet confined between two hard spheres located at the origin of the coordinate system and at position \mathbf{r} , respectively.

In order to take intermolecular interactions between the platelets into account we first calculate numerically the density profile $\rho(r, \omega)$ of platelets in an external potential of one fixed hard sphere of radius R_s . Thereafter the integral in Eq. (13) is evaluated by inserting this density profile. To our knowledge, this technique has not been used before for *interacting* nonspherical colloids acting as depletants.

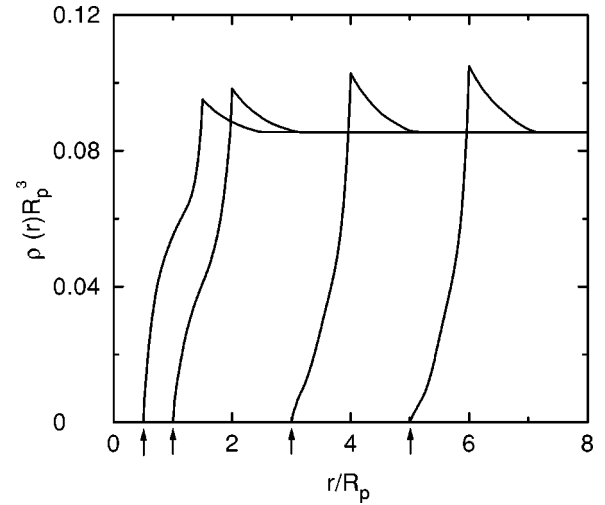


FIG. 5. Orientationally averaged density profile $\rho(r)$ as obtained from Eq. (14) for hard platelets of radius R_p in contact with a single hard sphere of radius R_s located at $r=0$. The radius of the sphere increases from left to right: $R_s/R_p=0.5, 1, 3, 5$. The arrows mark the location of the surface of the sphere at $r=R_s$. Since the platelets are arbitrarily thin their density is nonzero for $r > R_s$. All curves exhibit a cusp at $r=R_s+R_p$ followed by a decay towards the bulk density $\rho_b R_p^3=0.085$, which is essentially reached at $r=R_s+2R_p$. When the center of a platelet is located less than R_p from the sphere surface, there are fewer possible orientations available to the platelet.

The orientational averaged density profile

$$\rho(r) = \int d\omega \rho(r, \omega) \quad (14)$$

of the platelet fluid in contact with one fixed hard sphere is shown in Fig. 5 for various radii R_s of the sphere. Upon increasing $r \geq R_s$ from the surface of the sphere the averaged number density increases and exhibits a cusp at $r=R_s+R_p$ where platelets with their normal perpendicular to the radial direction touch the surface of the sphere with the rim. The maximum at the cusp is about 25% above the bulk value $\rho_b R_p^3=0.085$ for a size ratio $R_s/R_p=5$ and is less pronounced for smaller size ratios. The averaged density close to the surface of the sphere is larger for a small sphere than for a big one. Figure 6 displays the calculated depletion potential for two size ratios R_s/R_p as a function of the separation between the surfaces of the spheres $h=r-2R_s$. With decreasing size ratio the range and the depth of the primary minimum shrinks and the position of the small repulsive barrier observed at higher densities shifts to smaller values of h . Moreover, the height of the repulsive barrier decreases upon decreasing the size ratio. These results are due to the fact that the number of platelets contributing to the depletion potential decreases as the ratio of the radius of the spheres and the platelets becomes smaller at a fixed bulk density (see Fig. 5).

In agreement with a recent theoretical study [2] based on an evaluation of the excluded volume of a single platelet confined between two hard spheres, we find that the Derjaguin approximation for the depletion potential in the presence of noninteracting platelets yields accurate results for large size ratios $R_s/R_p > 1$. However, there are substantial

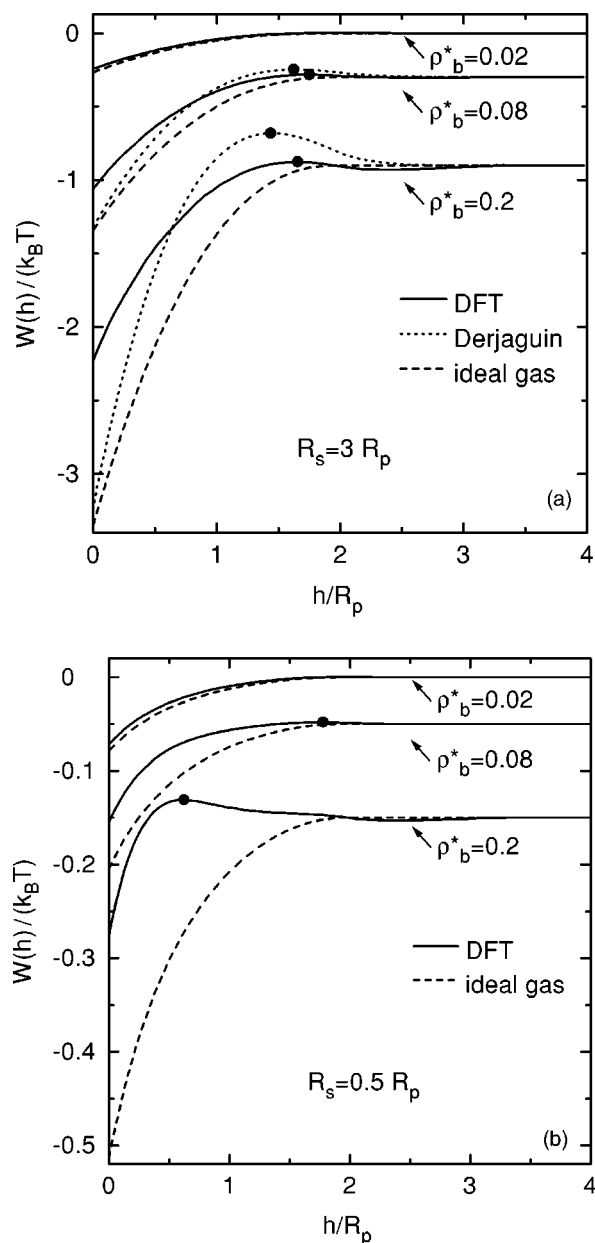


FIG. 6. Depletion potential $W(h)$ between two hard spheres of radius $R_s=3R_p$ in (a) and $R_s=0.5R_p$ in (b) due to the presence of thin hard platelets of radius R_p as obtained from Eq. (13). The bulk densities of the platelets are: $\rho_b^*=\rho_b R_p^3=0.02$ (top curves); $\rho_b^*=0.08$ (middle curves); $\rho_b^*=0.2$ (bottom curves). Here $h=r-2R_s$ is the separation between the surfaces of the spheres. The solid and dashed lines represent the calculations for interacting (DFT) and noninteracting platelets (ideal gas), respectively. In addition the depletion potential as obtained from the Derjaguin approximation [Eq. (5)] for interacting platelets is displayed by dotted lines in (a). For the smallest bulk density the solid and dotted line nearly coincide in (a). Since in (b) the spheres are only half as big as the platelets, in this case the Derjaguin approximation is unsuitable and therefore not shown. Only for sufficiently large densities a maximum denoted by a dot occurs. For reasons of clarity, the lower sets of curves are shifted down by $-0.3k_B T$ and $-0.9k_B T$, respectively, in (a) and by $-0.05k_B T$ and $-0.15k_B T$, respectively, in (b).

deviations at higher densities as can be seen from Fig. 6(a). The absolute value $|W(h=0)|$ of the DFT solution at contact is smaller than the one obtained from the Derjaguin approximation, and the repulsive barrier is less pronounced. For $R_s/R_p < 1$ and higher densities ρ_b the DFT results deviate strongly from the predictions for noninteracting platelets [see $\rho_b^*=\rho_b R_p^3=0.2$ in Fig. 6(b)].

In view of the significant difference between the DFT results and the Derjaguin approximation shown in Fig. 6(a) one may wonder if this is partly due to the fact that we have used the low-density functional [Eq. (13)] within the DFT framework. At the present stage we cannot answer this question since the next higher-order virial term contributing to the depletion potential would require the numerical evaluation of a ten-dimensional integral, which is beyond the scope of this study.

IV. SUMMARY

We have applied a density functional theory to fluids consisting of thin hard platelets confined between two hard spheres (Fig. 1). Within the framework of a second-order virial approximation of the excess free energy functional, the depletion potential between the two spheres due to the presence of the platelets is determined numerically and compared with the corresponding results for noninteracting platelets. The main conclusions which emerge from our study are as follows.

(1) Figure 2 demonstrate that steric interactions between thin platelets of radius R_p confined between two parallel hard walls increase the sum of the surface and finite-size contribution to the grand potential significantly already at rather low platelet densities $\rho_b R_p^3 \gtrsim 0.025$.

(2) As function of the slit width h the finite-size contribution to the grand potential of a slap of platelets exhibits a minimum at $h=0$ [Fig. 3(a)]. A maximum at larger values of h is found for higher platelet densities. The corresponding solvation force is attractive for small slit widths and exhibits a cusp at $h=2R_p$ [Fig. 3(b)].

(3) The depletion potential between two spheres as calculated from the Derjaguin approximation exhibits an attractive primary minimum at contact which deepens upon increasing the platelet density. Moreover, a small repulsive barrier at larger sphere separations develops with increasing density (Fig. 4). We find that the depletion barrier relative to zero is typically less than the thermal energy $k_B T$, and therefore unlikely to significantly alter the kinetics of aggregation of the hard spheres at platelet densities smaller than one half the density of the isotropic phase at bulk isotropic-nematic coexistence. Nonetheless, with increasing platelet density the integrated strength of the effective interaction between the spheres becomes significantly weaker and thus reduces the thermodynamic onset of flocculation.

(4) The orientational averaged density profile of a platelet fluid in contact with a single fixed hard sphere decreases towards the surface of the sphere because the range of accessible orientations is reduced when the particle approaches the

sphere. It exhibits a cusp at the position where the platelets lose contact with the surface of the sphere (Fig. 5). The maximum at the cusp decreases and the averaged density close to the surface increases as the ratio of the radius of the sphere and the platelets becomes smaller.

(5) With decreasing ratio of the radius of the spheres and the platelets, the primary minimum at contact and the small repulsive barrier of the depletion potential diminish and the position of repulsive barrier shifts to smaller values of the

separation of the surfaces of the spheres (Fig. 6). From our numerical results based on a density functional theory for a mixture of spheres and platelets we found that the Derjaguin approximation is valid for large size ratio and very small platelet density, but there are substantial deviations from the density functional results at higher densities [Fig. 6(a)]. For small size ratios and high platelet densities the ideal gas approximation for the platelets becomes unsuitable [Fig. 6(b), $\rho_b^* = 0.2$].

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